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Synthesis and Photophysical Properties of Pyrene-Based Light-Emitting Monomers: Highly Pure-Blue-Fluorescent, Cruciform-Shaped Architectures

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A new series of pyrene-based, pure-blue, fluorescent, stable monomers, namely 2,7-di-*tert*-butyl-4,5,9,10-tetrakis(*p*-R-phenylethynyl)pyrenes, have been successfully synthesised by Pd/Cu-catalysed Sonogashira coupling in excellent yield. The cruciform-shaped, π -conjugated structures were fully characterised by ¹H/¹³C NMR and IR spectroscopy, mass spectrometry and elemental analysis. As revealed from single-crystal X-ray analysis, there is a herringbone pattern be-

Introduction

In recent years, carbon-rich organic compounds with a high degree of π conjugation have received much attention because of their unique properties as ideal materials for advanced electronic and photonic applications, such as organic light-emitting diodes (OLEDs), liquid-crystal displays, thin-film transistors, solar cells and optical storage devices.^[1-3] Among them, functionalised, cruciform-shaped, conjugated fluorophores are well-known because they exhibit interesting optical and electronic properties due to their unique, multiply-conjugated-pathway structures. Examples of cruciform-shaped phores are the 1,2,4,5-tetrasubstituted (phenylethynyl)benzenes of Haley et al.,^[4] the X-shaped 1,2,4,5-tetravinyl-benzenes of Marks et al.,^[5] the 1,4-bis(arylethynyl)-2,5-distyrylbenzenes of Bunz et al.^[6] and other cross-shaped fluorophores developed by Nuckolls et al.^[7] and Scherf et al.^[8] In particular, the tetradonor-substituted (phenylethynyl)benzenes of Haley and coworkers showed excellent photophysical properties with the highest quantum yield. Therefore, their seminal studies on the structureproperty relationships for these materials provided valuable information for the molecular design of high-performance material.

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Pyrenes belong to the class of polycyclic aromatic hydrocarbons (PAHs) and have been widely used in many applications as fluorescent probes^[9] or fluorescent sensors^[10] by virtue of their excellent fluorescence properties. However, the use of pyrenes as emitters in OLEDs is limited because pyrenes easily form π aggregates/excimers in concentrated solution and the solid state, and the formation of π aggregates/excimers leads to long-wavelength excimer emission with low quantum efficiency. Recently, some pyrene derivatives have been developed as hole-transporting materials^[11] or host blue-emitting materials^[12] in OLEDs. Thus, there is substantial interest in designing and developing new pyrene-based blue-light-emitting molecules with high stability and efficiency for OLED applications.

Accordingly, our previous report on the synthesis of 4,5,9,10-tetrabromo-2,7-di-tert-butylpyrene^[13] prompted us to explore 4,5,9,10-tetrakis(phenylethynyl)pyrenes as emissive materials. We surmised that the sterically bulky tBu groups in pyrene rings at the 2- and 7-positions would help inhibit undesirable face-to-face π stacking in solution and the solid state.^[14] In addition to the ready synthetic accessibility by the Sonogashira coupling, the phenylacetylenic groups were a priori anticipated to facilitate the construction of the cruciform-shaped structure and further extend the conjugation length of the pyrene chromophore, resulting in a shift of the wavelength of absorption and fluorescence emission into the visible region of the electromagnetic spectrum.^[15] Herein, we report the synthesis and photophysical properties of a new series of pyrene-based, cruciform-shaped, π -conjugated, blue-light-emitting monomers with a low degree of π stacking in the solid state and pureblue emission by various spectroscopic techniques.

tween stacked columns, but the π - π stacking distance of adjacent pyrene units was not especially short at about 5.82 Å due to the introduction of the two bulky *t*Bu groups in the pyrene rings at the 2- and 7-positions. The photophysical properties of these monomers were carefully examined in different organic solvents, and these data strongly indicate their promising application as blue-emitting materials in organic light-emitting diodes (OLEDs).

Results and Discussion

Synthesis

Following our previous approach, we readily obtained 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (**2**) by the Lewis-acid-catalysed bromination of 2,7-di-*tert*-butylpyrene,^[13] (Scheme 1), and it served as the starting material for the synthesis of 4,5,9,10-tetrakis(*p*-R-phenylethynyl)pyrene derivatives.



Scheme 1. Synthesis of 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene (2). Reagents and conditions: (a) Br_2 , Fe powder, CH_2Cl_2 , room temp. for 4 h, 90%.

The modified Sonogashira coupling reaction of the tetrabromide **2** with various phenylacetylenes **3** produced the corresponding 2,7-di-*tert*-butyl-4,5,9,10-tetrakis(*p*-R-phenylethynyl)pyrenes **4** in excellent yields (recrystallisation yields) as light-green fluorescent solids (Scheme 2). As a comparison, we synthesised **5**, [1,3,6,8-tetrakis(4-methoxyphenylethynyl)pyrene] according to the literature procedure (Scheme 3).^[15]



Scheme 2. Synthesis of 4,5,9,10-tetrakis(phenylethynyl)pyrene derivatives **4a–c**. Reagents and conditions: (a) $[PdCl_2(PPh_3)_2]$, CuI, PPh₃, Et₃N/DMF (1:1), 24–48 h, 100 °C.

We fully determined the structures of these new pyrenes 4 and 5 by ¹H NMR, ¹³C NMR, FT-IR spectroscopy, mass spectroscopy as well as elemental analysis. Interestingly, al-



Scheme 3. Synthesis of 1,3,6,8-tetrakis[(4-methoxyphenyl)ethynyl]pyrene (5). Reagents and conditions: (a) [PdCl₂(PPh₃)₂], diisopropylamine, PPh₃, CuI, 24 h, 60–70 °C, 92%.

though we introduced the same numbers of *p*-functionalised phenylacetylenic groups into 4a-c and 5, their molecular structures were quite different, a result of introducing substituents at different positions on the pyrene scaffold. Compounds 4 and 5 also differ in the length and shape of their conjugation pathways. The ¹H NMR spectra of 4 and 5 were very simple due to their C_{2h} - and D_{2h} -symmetric structures, respectively. For example, 2,7-di-tert-butyl-4,5,9,10tetrakis(4-methoxyphenylethynyl)pyrene (4c) displayed a singlet at $\delta = 8.89$ ppm for the pyrene ring protons at the 1-, 3-, 6- and 8-positions, a pair of doublets in a 1:1 ratio at $\delta = 6.99$ and $\delta = 7.72$ ppm for the aromatic protons, a singlet at $\delta = 3.90$ ppm for the protons of the four MeO groups, and the protons of the two tBu groups appeared as a singlet at $\delta = 1.68$ ppm. Furthermore, the FT-IR spectra of 4 and 5 showed characteristic peaks at 2991-2961 (for C-H stretching of aliphatic segments), 2195-2198 (for $-C \equiv C$ -), ca. 1600, 1500 and 1460 (aromatic) cm⁻¹. In addition, 4c and 5 displayed strong absorption peaks at ca. 1170 and 1030 cm⁻¹ (for C–O–C stretching). Simultaneously, we also established the structures of 4 and 5 on the basis of the molecular ions at m/z 714, 939, 835 and 722 in their mass spectra, respectively. All results were consistent with the proposed cruciform-shaped structures (see the Supporting Information). The 4,5,9,10-tetrakis(phenylethynyl)pyrenes 4 were stable solids that could be stored in air at room temp. for a prolonged period of time. Compounds 4 had good solubility in all common organic solvents and high melting points up to 260 °C.

Molecular Structure and Crystal Packing of 4c

We further confirmed the molecular structure of **4c** by single-crystal X-ray analysis.^[16] We grew the crystals by slow evaporation of a CHCl₃/CH₂Cl₂ solution. We obtained

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this monomer as yellow needles, which provided excellentquality data. The crystallographic data for this monomer are presented in Table 1.

| Table 1. | Summary | of | the | crystal | data | of | 4 c. |
|----------|---------|----|-----|---------|------|----|-------------|
|----------|---------|----|-----|---------|------|----|-------------|

| Parameter | 4c |
|--|--|
| Empirical formula | $C_{60}H_{50}O_4$ |
| Formula weight [gmol ⁻¹] | 835.00 |
| Temperature [K] | 150(2) |
| Wavelength [Å] | 0.71073 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Crystal colour and size [mm] | yellow, $2.00 \times 0.05 \times 0.02$ |
| <i>a</i> [Å] | 12.865(3) |
| <i>b</i> [Å] | 5.9903(13) |
| <i>c</i> [Å] | 28.642(6) |
| a [°] | 90 |
| β [°] | 90.033(4) |
| γ [°] | 90 |
| Volume [Å ³] | 2207.3(8) |
| Ζ | 2 |
| Density, calcd. [g m ⁻³] | 1.256 |
| Absorption coefficient [mm ⁻¹] | 0.077 |
| <i>F</i> (000) | 884 |
| θ range for data collection [°] | 1.42 to 26.46 |
| Reflections collected | 18599 |
| Independent reflections | 4544 |
| Observed data $[F^2 > 2\sigma(F^2)]$ | 2297 |
| R _{int} | 0.1134 |
| Restraints/parameters | 0/295 |
| Goodness-of-fit on F^2 | 0.978 |
| $R1 [F^2 > 2\sigma(F^2)]$ | 0.0566 |
| wR2 (all data) | 0.1463 |

Structure diagrams of **4c** are shown in Figure 1. The molecule lies on a two-fold axis; thus, half is crystallographically unique. The four ethynyl carbons are essentially coplanar with the central pyrene ring, while the four C_6H_4 rings are not coplanar with the central pyrene ring but have twist angles of 18.3° for ring C(15)–C(20) and 23.6° for ring C(24)–C(29), relative to the central, pyrene core. In addition, the relative twist angle between these two C_6H_4 groups was 39.5°. The methoxyl groups were twisted by 14.6° and 2.5° relative to their respective rings of attachment.

The crystal packing of pyrene molecules has been studied previously. A card-packed structure was observed, and the molecules exhibited an interplanar separation of ca. 3.5 Å with strong π - π stacking through the involvement of 14 carbons in each pyrene molecule.^[17] As shown in Figure 2, the present cruciform-shaped molecules of 4c are packed in a herringbone arrangement in the crystal. In addition, each 4c molecule displays a 24-point, π - π stacking interaction with molecules above and below (Figure 2, structure i) using both the pyrenyl carbons and phenylethynyl carbons for both interactions. Interestingly, the closest intermolecular C-C distance between the central pyrenyl planes of two adjacent 4c molecules is not especially short at about 5.82 Å in this crystal lattice. These results strongly indicate that the two bulky tBu groups attached to the pyrene rings at the 2- and 7-positions play an important role in suppressing the undesirable, face-to-face, π - π stacking in the solid state.



Figure 1. X-ray crystal-structure diagrams of 4c (i) top view; (ii) side view.



Figure 2. Packing diagrams of **4c**: (i) view parallel to *b*, highlighting the π - π stacking; (ii) view parallel to *c*, showing the herringbone packing motif.

Hence, because efficient π stacking in emitting molecules can lead to extensive excimer formation in the solid state or in thin films, with a consequent shift in the emission spectrum and a reduction in the quantum yield of fluorescence,^[18] the low degree of π stacking in the crystal lattice in these current pyrene-based monomers **4** suggests that they should be robust blue-light-emitting materials.

Photophysical Properties

We measured the UV/Vis absorption and fluorescence spectroscopic data of these new pyrenes with cruciformshaped conjugation in dilute CH₂Cl₂ solution at room temp. and the results are presented in Table 2, together with those of pyrenes 1 and 5. The normalised UV/Vis absorption spectrum is shown in Figure 3. For pyrene 1, the absorption spectra was almost identical to that of the parent pyrene,^[19] with three well-resolved, sharp, absorption bands observed in the 300-350 nm region. The slight bathochromic shift (ca. 3 nm) we ascribe to the increased π -electron density on the pyrene ring, arising from the electron-donating nature of the two tBu groups at the 2- and 7-positions.^[20] In contrast, the optical absorption spectrum of 5 was very broad and less well resolved. The longest wavelength band was substantially bathochromically shifted by ca. 140 nm in comparison to pyrene 1 due to the extended conjugation length of the pyrene chromophore with the phenylacetylenic units at the 1-, 3-, 6- and 8-positions. In addition, it reveals a vibronic feature characteristic of the unsubstituted parent pyrene with a short-wavelength absorption maximum at ca. 350 nm and the conjugation segments with a long wavelength absorption maximum at ca. 480 nm.

Table 2. Optical absorption and emission spectroscopic data for **4a–c** in CH₂Cl₂ (ca. 10^{-5} – 10^{-6} M) and room temp., compared with that of pyrenes 1 and 5.^[a]

| Entry | | Absorption λ_{abs} [nm] | [b] ε [M ⁻¹ cm ⁻¹] | Fluorescence ^[c] $\lambda_{max} [nm] (\lambda_{ex})^{[d]}$ | Stokes [cm ⁻¹] | shift $\Phi_{\mathrm{f}}^{\mathrm{[e]}}$ |
|--------|----------|---------------------------------|--|--|----------------------------|--|
| 1 | 1 | 339 | 26300 | 378 (252) | 3043 | 0.12 |
| 3 | ча 4b | 413 | 38900 | 448 (328) | 1892 | 0.00 |
| 4 5 | 4c 5 | 415 477 | 45700 88900 | 453 (333) 496 (260) | 2021 803 | 0.98 0.96 |

[a] All measurements were performed under degassed conditions. [b] λ_{abc} is the absorption band appearing at the longest wavelength at $\approx 10^{-5}$ M in CH₂Cl₂. [c] λ_{ex} is the fluorescence band appearing at the shortest wavelength at $\approx 10^{-6}$ M in CH₂Cl₂. [d] Wavelength of excitation. [e] Fluorescence quantum yields; the values (±0.01– 0.03) are relative to that of diphenylanthracene (0.90 in cyclohexane).

On the other hand, compared with that of pyrene 1, all the UV/Vis absorption spectra of 4a–c were broad and less well-resolved, and the longest–wavelength, π - π *, absorption maximum of 4a, 4b and 4c occurred at 410, 413 and 415 nm, respectively (Table 2); these bands were bathochromically red-shifted by 71–76 nm from the corresponding band of 1 as a result of the extended conjugation length of the pyrene chromophore with the phenylacetylenic units



Figure 3. Normalised UV/Vis absorption spectra of 4 recorded in CH_2Cl_2 at about 10^{-5} M and 25 °C, compared with those of pyrenes 1 and 5.

introduced at the 4-, 5-, 9- and 10-positions. Interestingly, although the vibronic features of **4a–c** were more similar to those of 5 than to those of 1 (Figure 3), the spectra of 4 were less red-shifted than that of 5, despite the presence of the two electron-donating tBu groups in $5^{[20]}$ A reasonable explanation for these different shifts between 4 and 5 is their quite different conjugation pathways. For 4, the four phenylacetylenic units are connected with the central pyrene moieties at the nearby 4-, 5-, 9- and 10-positions to afford a short, cruciform, π -conjugated, molecular structure. Hence, short, cruciform, π conjugation occurs; for 5, however, these four phenylacetylenic units are connected with pyrene moieties at the more distant 1-, 3-, 6- and 8positions, resulting in a longer cruciform, π -conjugated structure. Hence, the conjugation length of 5 is larger than that of 4, which leads to a larger red-shift to ≈ 500 nm. Additionally, among 4a-c, the [(p-methoxyphenyl)ethynyl]pyrene 4c displayed the largest bathochromic shift of the absorption bands, which could be attributed to the methoxy group having the strongest electron-donating ability of the three different substituents.

Upon excitation, a dilute solution (ca. 10^{-6} M) of 4 and 5 in CH₂Cl₂ at room temp. showed pure-blue and green emission, respectively (Figure 4). For example, compared with the lowest-energy emission band of pyrene 5 at 496 nm, the lowest-energy emission band of 4a, 4b and 4c occurred at 441, 448 and 453 nm, respectively. The fluorescence emission bands of 4a, 4b and 4c were almost identical. Only one emission band was observed in the visible pure-blue region, which indicated all these emissions occur from the lowest excited state with the largest oscillator strength. All spectra are bathochromically red-shifted into the pure-blue visible region. Additionally, the fluorescence spectra of these cruciform-shaped compounds systematically varied in agreement with the electronic absorption spectra, implying that the energy gap between the ground and excited states decreases in the order of 4a > 4b > 4c (Table 2). The fluorescence spectra were independent of the excitation wavelength. The fluorescence Stokes shifts increased in the order of 4a < 4b < 4c. The fluorescence quantum yields of 1, 4a-c and 5 recorded in dilute CH₂Cl₂ solution at room temp. are also listed in Table 2. We found the Φ_f values of 1, 4a-c and 5 to be in the range of 0.12–0.98 relative to that of 9,10-diphenylanthracence (0.90 in cyclohexane).^[21]



Figure 4. Normalised fluorescence emission spectra of 4a-c and 5 recorded in CH₂Cl₂ at ca. 10⁻⁶ M and 25 °C.

We emphasise that several reported 1,3,6,8-tetrakis(phenylethynyl)pyrenes^[15] show very low values of quantum efficiency in solution due to the possibility that free rotation of the phenyl substituents in conjugation with the central pyrene chromophore would allow competing nonradiative pathways for the decay of the excited singlet state. Interestingly, in the current cruciform-shaped 4 and 5, all compounds had dramatically high quantum yields. Even though 4 and 5 share this potential for nonradiative decay, they differ in important ways from previously reported structures. Compounds 4a-c have a short, cruciform-shaped structure, similar to that of the tetra-donor-substituted (phenylethynyl)benzenes of Haley and coworkers.^[4c] Compound 5 contains strongly electron-donating methoxyl groups.^[15] These structural differences relative to the lowquantum-yield structures provide good explanations for the high quantum yields observed.

Pyrene itself did not exhibit excimer emission at a concentration of 10^{-5} M and below, but both 1-(phenylethynyl)pyrenes^[22] and a 1,3,6,8-tetrakis(phenylethynyl)pyrene^[15] showed excimer emission at 10^{-5} M and even higher concentrations. Therefore, we examined the effect of concentration on the fluorescence emission of **4c** in CH₂Cl₂. By increasing the concentration from 1.0×10^{-8} M (Figure 5, line 1) to 1.0×10^{-4} M (Figure 5, line 9), we observed the intensity of this emission band to gradually increase, and we observed the emission corresponding to only the monomer at 453 nm (Figure 5). This evidence also indicated that the attachment of sterically bulky *t*Bu groups at the 2- and 7-positions can prevent two molecules of **4** from getting close enough to result in excimer emission at high concentrations.



Figure 5. Effect of concentration on the fluorescence emission spectra of **4c**, recorded in CH₂Cl₂ at room temp. (1) 1.0×10^{-8} M, (2) 2.5×10^{-8} M, (3) 1.0×10^{-7} M, (4) 2.5×10^{-7} M, (5) 1.0×10^{-6} M, (6) 2.5×10^{-6} M, (7) 5.0×10^{-6} M (8) 2.5×10^{-5} M and (9) 1.0×10^{-4} M. $\lambda_{ex} = 333$ nm.

In order to obtain more insight into the photophysical properties of these new cruciform-shaped, conjugated pyrenes 4, we examined the normalised absorption spectra and emission spectra of 4a and 4c in various solvents, and the optical data are summarised in Table 3. It is well-known that the solvatochromic effect is not only dependent on molecular structure but also on the nature of the chromophore and the solvent.^[23] Each monomer showed a certain solvatochromism in both the absorption and the emission spectrum. For example, for 4c, a change of solvent from nonpolar cyclohexane to polar DMF caused only a very slight, positive, bathochromic shift in the π - π * absorption band from 413 to 417 nm (Figure 6). On the other hand, in the case of the emission spectrum of 4c, we observed a substantial positive bathochromism with a peak around 425 nm and a shoulder around 450 nm in cyclohexane (Figure 7), while we observed a broad and red-shifted emission with

Table 3. Optical absorption and emission spectroscopic data for 4a and 4c in various solvents (ca. $10^{-5}-10^{-6}$ M) at room temp.^[a]

| | 4a | | | | 4c | 4c | | | |
|---------------------------------|----------------------------------|--|-------------------------------------|-------------------------|------------------------------------|--|-------------------------------------|---------------------------|--|
| Solvent | $\lambda_{abs max}$ $[nm]^{[b]}$ | $\lambda_{\rm em \ max}$ [nm] ^[c] | Stokes shift [cm ⁻¹] | $arPhi_{ m f}^{ m [d]}$ | $\lambda_{ m abs\ max} [nm]^{[b]}$ | $\lambda_{em max}$ [nm] ^[c] | Stokes shift [cm ⁻¹] | $arPhi_{ m f}^{[{ m d}]}$ | |
| Cyclohexane | 408 | 419 | 643 | 0.58 | 413 | 425 | 684 | 0.73 | |
| THF | 410 | 424 | 746 | 0.62 | 415 | 435 | 1050 | 0.84 | |
| CH ₂ Cl ₂ | 411 | 441 | 1714 | 0.66 | 416 | 453 | 2021 | 0.98 | |
| DMF | 412 | 449 | 2000 | 0.60 | 417 | 464 | 2429 | 0.82 | |

[a] All measurements were performed under degassed conditions. [b] λ_{abs} is the absorption band appearing at the longest wavelength at about 10⁻⁵ M in the different solvents. [c] λ_{ex} is the fluorescence band appearing at the shortest wavelength at about 10⁻⁶ M in the different solvents. [d] Fluorescence quantum yields; the values (±0.01–0.03) are relative to that of diphenylanthracene (0.90 in cyclohexane).

only one peak at $\lambda_{max} = 464$ nm in the solvent of high polarity, DMF. We also observed similar results for 4a in both the absorption and emission spectra (see the Supporting Information). Although the dipole moments of 4a-c in either the ground or excited states were indeed zero because they possess C_{2h} symmetry, the results obtained above indicated that the Q_e (the quadrupole moments of 4 in the excited state) should be larger than the Q_g (the quadrupole moments of 4 in the ground state) because we observed positive solvatochromic effects in both the absorption and the emission spectra; this implies that there is a change in the quadrupole moment upon excitation.^[24] On the other hand, the fact that solvatochromic effects are more important for emission than for absorption suggests that these new pyrenes 4 are more solvated in the excited state than in the ground state.^[25]



Figure 6. Normalised absorption spectra of 4c recorded in (a) cyclohexane, (b) THF, (c) CH_2Cl_2 and (d) DMF at ca. 10^{-5} M and 25 °C.



Figure 7. Normalised fluorescence spectra of 4c recorded in (a) cyclohexane, (b) THF, (c) CH_2Cl_2 and (d) DMF at ca. 10^{-6} M and 25 °C.

Conclusions

By using a modified Sonogashira coupling reaction, we have prepared a new series of well-defined, pyrene-based



monomers with cruciform-shaped, π -conjugated structures in excellent yield and fully characterised the special cruciform-shaped structures. The results obtained through inspecting the absorption and emission spectra of these pure monomers, indicate that the extension of π conjugation in these pyrene chromophores through phenylacetylenic substituents serves to shift the wavelength of absorption and fluorescence emission into the pure-blue visible region. Single-crystal X-ray analysis indicated the two bulky tBu groups on the pyrene molecule at the 2- and 7-positions play a very important role in inhibiting the π -stacking interactions between neighbouring pyrene units. These molecules emit very bright, pure-blue fluorescence and have good solubility in common organic solvents and high stability. Hence, they are promising as blue organic light-emitting materials for the fabrication of OLED devices.

Experimental Section

Genenal Remarks: All melting points are uncorrected. The ¹H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with TMS as an internal reference. The IR spectra were obtained as KBr pellets with a Nippon Denshi JIR-AQ2OM spectrometer. UV/ Vis spectra were obtained with a Perkin–Elmer Lambda 19 UV/ Vis/NIR spectrometer in various organic solvents. Fluorescence spectroscopic studies were performed in various organic solvents in a semimicro fluorescence cell (Hellma[®], 104F-QS, 10×4 mm, 1400 µL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were measured using absolute methods. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyser.

Materials: The preparation of 2,7-di-*tert*-butylpyrene (1) was described previously.^[13]

Acid-Catalysed Bromination of 2,7-Di-*tert*-butylpyrene: To a mixture of 2,7-di-*tert*-butylpyrene (500 mg, 1.60 mmol), CH₂Cl₂ (250 mL) and Fe powder (250 mg), a solution of Br₂ (1,400 mg, 8.7 mmol) in CH₂Cl₂ (25 mL) was added dropwise over 1 h at 0 °C with stirring. After this addition, the mixture was warmed to room temp. and stirred for 4 h. The mixture then was poured into a large amount of ice-water and extracted with CH₂Cl₂ (250 mL). The organic extracts were washed with aqueous Na₂S₂O₃ (10%), water and brine, dried (Na₂SO₄), and the solvents were evaporated. The residue was dissolved in CH₂Cl₂ and purified by column chromatography, eluting with hexane, to give a pale-yellow solid (980 mg, 90%); m.p. 286–288 °C (ref.^[13] 286–288 °C). ¹H NMR (300 MHz, CDCl₃): δ = 1.62 (s, 18 H, *t*Bu), 8.87 (s, 4 H, pyrene-*H*) ppm.

General Procedure for the Sonogashira Coupling Reaction Towards the Synthesis of 4a–c: 4,5,9,10-Tetrabromo-2,7-di-*tert*-butylpyrene 2 (0.32 mmol), [PdCl₂(PPh₃)₂] (0.016 mmol), CuI (0.016 mmol), PPh₃ (0.032 mmol) and a phenylacetylene (2.56 mmol) were added to a degassed solution of DMF (10 mL) and Et₃N (10 mL) under argon. The resulting mixture was stirred at 100 °C for the time mentioned in the individual cases. The reaction mixture was then cooled to room temp. and quenched with Et₂O and extracted. The solvent was removed to give the crude reaction mixture, which was further worked up as indicated in the individual cases. 2,7-Di-tert-butyl-4,5,9,10-tetrakis(phenylethynyl)pyrene (4a): To a stirred solution of 4,5,9,10-tetrabromo-2,7-di-tert-butylpyrene (2, 200 mg, 0.32 mmol), Et₃N (10 mL) and DMF (10 mL), was added [PdCl₂(PPh₃)₂] (12 mg, 0.016 mmol), CuI (3.2 mg, 0.016 mmol) and PPh₃ (8.2 mg, 0.032 mmol), and the mixture was stirred for 30 min at 0 °C under argon. Phenylacetylene (260 mg, 2.56 mmol) was then added, and the mixture was heated to 100 °C with stirring for 24 h. After it was cooled, the mixture was diluted into Et₂O (150 mL) and washed successively with saturated aqueous NH₄Cl, H₂O and brine. The organics were dried (MgSO₄), and the solvents were evaporated. In order to obtain pure product, the crude product was purified twice by column chromatography, eluting with hexane/CH2Cl2 (9:1), and recrystallised from hexane to afford the desired compound as pale-green prisms (149 mg, 65%); m.p. > 300 °C. IR (KBr): ṽ = 2961, 2197 (−C≡C−), 1597, 1493, 1442, 1362, 877, 755, 690, 561, 530 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 1.69 (s, 18 H, tBu), 7.45–7.54 (m, 12 H, Ar-H), 7.80 (d, J = 8.7 Hz, 8 H, Ar-H), 8.93 (s, 4 H, pyrene-H) ppm. ¹³C NMR (75 MHz, $CDCl_3$): $\delta = 149.8, 131.8, 129.5, 128.7, 128.6, 124.1, 123.7, 123.0,$ 121.3, 99.6, 87.8, 35.7, 32.0 ppm. FAB-HRMS: calcd. for C₅₆H₄₂ [M]⁺ 714.92; found 714.38. C₅₆H₄₂ (714.38): calcd. C 93.62, H 5.38; found C 93.59, H 5.90.

2,7-Di-tert-butyl-4,5,9,10-tetrakis[(4-tert-butylphenyl)ethynyl]pyrene (4b): To a stirred mixture of 4,5,9,10-tetrabromo-2,7-di-tert-butylpyrene 2 (200 mg, 0.32 mmol), Et₃N (10 mL) and DMF (10 mL), was added [Pd(PPh₃)₂Cl₂] (12 mg, 0.016 mmol), CuI (3.2 mg, 0.016 mmol) and PPh₃ (8.2 mg, 0.032 mmol), and the mixture was stirred for 30 min at 0 °C under argon. (4-tert-Butylphenyl)acetylene (404 mg, 2.56 mmol) was then added to the mixture, which was heated to 100 °C with stirring for 48 h. After it was cooled, the mixture was diluted into Et₂O (200 mL) and washed successively with saturated aqueous NH₄Cl, H₂O and brine. The organics were dried (MgSO₄), and the solvents were evaporated. The crude product was purified by column chromatography, eluting with hexane/ ethyl acetate (9:1), and recrystallised from hexane to give the desired product as pale-green prisms (204 mg, 68%); m.p. > 300 °C. IR (KBr): $\tilde{v} = 2962, 2198$ (-C=C-), 1601, 1516, 1505, 1464, 1394, 1363, 1327, 1268, 1247, 1096, 1016, 880 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 1.40 (s, 36 H, tBu), 1.68 (s, 18 H, tBu), 7.49 (d, J = 8.2 Hz, 8 H, Ar-H), 7.74 (d, J = 8.5 Hz, 8 H, Ar-H), 8.92 (s, 4 H, pyrene-*H*) ppm. ¹³C (75 MHz, CDCl₃): δ = 152.0, 149.7, 131.6, 129.6, 125.6, 124.0, 122.8, 121.2, 120.7, 99.8, 87.3, 35.6, 34.9, 32.0, 31.3 ppm. MS (EI): m/z 939.36 [M]⁺. C₇₂H₇₄ (938.60): calcd. C 92.06, H 7.94; found C 92.02, H 8.01.

2,7-Di-tert-butyl-4,5,9,10-tetrakis[(4-methoxyphenyl)ethynyl]pyrene (4c): To a stirred mixture of 4,5,9,10-tetrabromo-2,7-di-tert-butylpyrene 2 (200 mg, 0.32 mmol), Et₃N (10 mL) and DMF (10 mL), was added [PdCl₂(PPh₃)₂] (12 mg, 0.016 mmol), CuI (3.2 mg, 0.016 mmol) and PPh₃ (8.2 mg, 0.032 mmol), and the mixture was stirred for 30 min at 0 °C under argon. 4-Ethynylanisole (340 mg, 2.56 mmol) was then added, and the mixture was heated to 100 °C with stirring for 48 h. After it was cooled, the mixture was diluted into Et₂O (150 mL) and washed successively with saturated aqueous NH₄Cl, H₂O and brine. The organics were dried (MgSO₄), and the solvents were evaporated. The crude product was purified by column chromatography, eluting with a mixture of hexane/CH2Cl2 (5:1), and recrystallised from ethyl acetate to afford the pure desired compound as a pale-green solid (200 mg, 75%); m.p. 262-264 °C. IR (KBr): ṽ = 3479, 2991, 2195 (−C≡C−), 1606, 1568, 1557, 1511, 1505, 1456, 1410, 1362, 1290, 1249, 1170, 1104, 1030, 943, 898, 816, 557 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 1.68 (s, 18 H, *t*Bu), 3.90 (s, 12 H, OMe), 6.99 (d, *J* = 8.5 Hz, 8 H, Ar-*H*), 7.72 (d, J = 8.5 Hz, 8 H, Ar-H), 8.89 (s, 4 H, pyrene-H) ppm. ¹³C (75 MHz,

CDCl₃): δ = 160.0, 149.9, 143.1, 133.2, 129.6, 123.8, 123.0, 116.4, 114.3, 99.8, 86.8, 55.4, 35.6, 32.0 ppm. MS (EI): *m*/*z* 835.04 [M]⁺. C₆₀H₅₀O₄ (834.40): calcd. C 86.30, H 6.04, O 7.66; found C 86.15, H 6.10, O 7.56.

1,3,6,8-Tetrakis[(4-methoxyphenyl)ethynyl]pyrene (5):^[15] 1,3,6,8-Tetrabromopyrene (200 mg, 0.39 mmol), [PdCl₂(PPh₃)₂] (14 mg, 0.0195 mmol), CuI (4 mg, 0.0195 mmol), PPh₃ (10 mg, 0.039 mmol) and 4-ethynylanisole (412 mg, 3.12 mmol) were added to a degassed solution of diisopropylamine (10 mL) and THF (10 mL) under argon. The resulting mixture was heated at 70 °C with stirring for 24 h. After the mixture was cooled, the red-orange precipitate was filtered and washed with CHCl₃ (50 mL) and benzene (50 mL) and then recrystallisation from CHCl₃ to afford the pure desired compound as a red-orange powder (259 mg, 92%); m.p. 236–238 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.89 (s, 12 H, OMe), 6.97 (d, J = 9.0 Hz, 8 H, Ar-H), 7.67 (d, J = 8.7 Hz, 8 H, Ar-H), 8.40 (s, 2 H, pyrene- $H_{2,7}$), 8.74 (s, 4 H, pyrene- $H_{4,5,9,10}$) ppm. ¹³C NMR of this compound could not be determined due to its low solubility. MS (EI): m/z 722.82 [M]⁺. C₅₂H₃₄O₄ (722.35): calcd. C 86.41, H 4.74, O 8.85; found C 86.35, H 4.75, O 8.90.

Crystal Data and Refinement Details for 4c: Diffraction data were collected using a Bruker SMART APEX II CCD diffractometer using narrow frames to $\theta_{max} = 26.46^{\circ}$.^[26] Data were corrected for absorption on the basis of symmetry-equivalent and repeated data (minimum and maximum transmission factors: 0.861, 0.999) and Lp effects. The structure was solved by direct methods and refined on F^2 using all the data.^[27] H atoms were constrained in a riding model. Further details can be found in Table 1 and ref.^[16]

Supporting Information (see also the footnote on the first page of this article): ¹H NMR spectra of compounds **4a–4c** and **5**, UV/Vis spectra of **4a**, fluorescence spectra of **4a**.

Acknowledgments

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